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THE STATE OF GAS BEHIND A STRONG SHOCK WAVE

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ABSTRACT

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Derivation of a system of kinetics and gas-dynamics equations determining the state of a gas behind strong shock waves. A method of solution is proposed which takes into account the presence of all the excited states of neutral atoms. Relaxation in air is investigated for shock-wave velocities $v_1 > 10$ km/sec. The fundamental processes are ascertained, and the relaxation times are calculated.

Author
A study of the state of gas behind a shock-wave front demands the /340* simultaneous solution of equations involving gas dynamics and physical and chemical kinetics. There are difficulties associated with the necessity of taking into consideration the numerous chemical compounds formed during the relaxation process, as well as the aggregate of excited states of the various atoms and molecules (Ref. 1,2).

This paper makes note of a suitable system of equations and proposes

*Note: Numbers in the margin indicate pagination in the original foreign text.

an approximate method for solving it with due regard for the role of the excited states.

Specifically, a shock wave in air at velocities of $v_1 \geq 10$ km/sec is examined. Despite the approximate nature of the solution, the results obtained, it seems to us, are essentially general in nature.

1. Previous estimates (Ref 3) are confirmed which state that dissociation occurs rather rapidly behind a shock wave (at $v_1 \geq 10$ km/sec for air), while the length of the relaxation zones is determined by ionization processes. This is in direct conflict with the low velocity case, when the degree of ionization increases comparatively rapidly, and comes into equilibrium with a state of unbalanced dissociation, after which it follows the change in this dissociation (Ref 4).

2. A non-monotonic change in length of the ionization relaxation zone takes place as a function of shock wave velocity. In the $v_1 = 9 \div 10$ km/sec range, the length of this zone increases with an increase in v_1 .

Basic Equations

If the shock wave velocity is sufficiently high, there are practically no molecules in the equilibrium zone behind the shock-wave front. The appendix shows, with reference to air, that under these conditions dissociation occurs much more rapidly than ionization. At $v_1 \geq 10$ km/sec, this enables us to regard relaxation in air as relaxation in a mixture of atomic gases*.

We shall write the basic equations for planar shock waves in a single-

*The same result occurs for other, molecular gases, but the boundary value of v_1 may be different.

constituent gas whose atoms are principally to be found in various /341 excited states. There are no basic difficulties in extending the results to mixtures of gases.

If the wave is stationary, the balance of the number of particles at the k^{th} level of the atom has the form:

$$\begin{aligned}
 -\frac{d}{dx}(n_k v) = & (n_k n_e j_{ke}^e - n_e^2 n_k j_{ke}^e) + \sum_n (n_k n_{en} - n_n n_{ek}) + \\
 & + P_k - a_{ek} n_e n_k + \sum_n (n_k n_n j_{kn}^m - n_n n_k j_{kn}^m) + \sum_n (n_k n_n j_{kn}^m - \\
 & - n_n n_k n_n j_{kn}^m) + \sum_{m,n} (n_k n_n j_{kn}^m - n_n n_k j_{kn}^m).
 \end{aligned}
 \tag{1}$$

The left side of (1) accounts for the transport of atoms in the flux; v is the velocity relative to the front; x is the distance from the front. The right side pertains to collisions and radiation processes. Atoms of the k^{th} level are ionized by collisions with electrons with efficiency j_{ke}^e , and with atoms on the m^{th} level - for example, with efficiency j_{ke}^m . The two values j_{ek}^e and j_{ek}^m accordingly account for the opposing processes; j_{kn}^e is the probability of $k \rightarrow n$ excitation by electronic impact ($k < n$), or by impact of the second kind ($n < k$); j_{kn}^m is the probability of similar processes on collision with atoms in the m^{th} state; a_{ek} , the probability of photo-recombination; $a_{kn} + A_{kn}$, the probability of spontaneous $k \rightarrow n$ transition, $a_{kn} = 0$, if $k \leq n$ or level k is metastable. Summation is carried out on all the levels realized in the plasma. Electron concentration is denoted by n_e , and P_k is the integral term which makes allowance for the formation and destruction of the k^{th} state during absorption of radiation of the remaining gas volume.

The kinetic electron temperatures T_e , and atom and ion temperatures T_a , are not identical; T_e are found from the energy balance of the electron

gas*:

$$\frac{d}{dx} \left(\frac{3}{2} k T_e n_e v \right) + k T_e n_e \frac{dv}{dx} = S_{ee} + \frac{d}{dx} \left(\chi_e \frac{dT_e}{dx} \right), \quad (2)$$

where S_{ee} is the source of electron energy and χ_e is the coefficient of electron heat conductivity. Since the gas parameter gradients behind the front are comparatively small, the transfer processes are not significant. Electron heat conductivity is known to occupy a special position, and must be taken into account in some cases.

We employ the symbol S_{ee} to designate electron heating in elastic collisions ($\sum'_m n_m n_e Q_{me}$; summation was made over all the states of all gas particles) and in radiation absorption W_{ee} (during free-free transitions and /342 photo-ionization), losses in free-free transitions ($\sum'_m n_m n_e F_{me}$) and inelastic collisions:

$$\begin{aligned} S_{ee} = & - \sum_k (U_i - U_k) (n_k n_e f_{ke} - n_e^2 n_i f_{ek}) - \frac{1}{2} \sum_{k, n} (U_n - U_k) (n_k n_e f_{kn} - \\ & - n_n n_e f_{nk}) + \sum_{k, m} (\varphi_{km} n_k n_m f_{km} - \varphi_{km}' n_e n_i n_m f_{ek}^m) - \\ & - \sum_k \varphi_k n_e n_e U_i + W_{ee} + \sum_m n_m n_e (Q_{me} - F_{me}), \end{aligned} \quad (3)$$

where U_i is ionization energy from the basic state; U_k , excitation energy of the k^{th} level; $\varphi_{km}(T_a)$, average energy with which an electron is produced in atom-atom collisions; and $\varphi_{km}(T_a, T_e)$ and $\varphi_k(T_e)$ represent the average loss of energy in electron gas per recombination event.

The kinetics equations are solved simultaneously with the conservation equations which take losses by radiation Q into account. In standard notation,

* The energy balance of an electron gas, in general terms, has the following aspect:

$$\frac{d}{dx} \left(\frac{3}{2} k T_e n_e v_e \right) + k T_e n_e \frac{dv_e}{dx} = S_{ee} + \frac{d}{dx} \left(\chi_e \frac{dT_e}{dx} \right),$$

where v_e is electron velocity which is different from heavy particle velocity v . Under the conditions we investigated, however, the difference between v_e and v is small.

we have:

$$\rho v = \rho_1 v_1; \quad p + \rho v^2 = p_1 + \rho_1 v_1^2; \quad \frac{d}{dx} \left(H + \frac{v^2}{2} - \kappa_e \frac{dT_e}{dx} \right) = - \frac{Q}{\rho v}. \quad (4)$$

Subscript 1 refers to the gas before the front. Let us write the equation for Q:

$$Q = \sum_{k, n} (U_n - U_k) a_{nk} n_k + \sum_k (U_i - U_k + \varphi_k) a_{ek} n_e n_i + \\ + \sum_{m'} n_n n_e F_{me} - \sum_{k, n} (U_k - U_n) P_{kn} - \sum_k (U_i - U_k) P_{ke} - W_{ee}. \quad (5)$$

Excitation during radiation absorption ($k \rightarrow n$) is taken into consideration by P_{kn} . In photoionization, one part of the energy [represented by $\sum (U_i - U_k) P_{ke}$] goes to detach the electron and another to impart kinetic energy to it. The second quantity entered into equation (3) and was represented by W_{ee} . Let us note that in some cases a noticeable contribution to Q may be made by radiation processes not considered in equation (5), in order not to make it unnecessarily cumbersome. The role of these processes behind a shock-wave in air is discussed further on.

In addition to ordinary ions n_i , the plasma contains molecular ions n_2^+ . The bond between them is effectuated by a very rapid process of charge exchange. The ions are therefore in quasi-equilibrium. If, moreover, we consider that atom and molecule combinations are also interconnected by an equilibrium condition (dissociation relaxation having come to an end), we then obtain

$$n_2^+ = K n_i n_2, \quad (6)$$

where K is the equilibrium constant of reaction $A_2^+ \rightleftharpoons A^+ + A$. With regard to equation (6), we use coefficients such as j_{ke}^m and j_{ek}^m to write the velocities of associative ionization and dissociative recombination, as these processes are noted in equations (1), (3), and (5).

The plasma is quasi-neutral, i.e., $n_e = n_1 + n_2^+$. In reality, there is a charge separation, but separation length is slight and diffusion is ambipolar.

Absorption of the leading radiation upsets the equilibrium of the gas before the front, and thus establishes the initial conditions of relaxation (Ref. 3).

Method of Solving a System of Kinetic Equations

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The system derived is very cumbersome, but any approximate method of solving it must take into consideration the whole set of excited states of the active atom.

Let us note that contiguous states are very intimately interrelated by shock processes (very large cross-sections and similar energy values). Therefore, all the various causes of deviation from equilibrium may change the total population of these states, rather than the relative distribution of particles among them. Radiation yield, for example, while considerably decreasing the total concentration of excited atoms and electrons, does not disturb particle distribution within this set of states (Ref. 5). In (Ref. 5), the nonclosed nature of the system was the sole reason for deviation from equilibrium. Behind the shock-wave, the lack of equilibrium is chiefly the result of a gas parameter jump at the front, but for the same reason the relaxation within the set of neighboring excited states proceeds very rapidly. Therefore, particle distribution within the set of contiguous states (in which we will also include the continuous spectrum) is determined by the following system of equations:

$$\begin{aligned}
& (n_k n_e j_{ke} - n_e^2 n_i j_{ek}) + \sum_n (n_k n_e j_{kn} - n_n n_e j_{nk}) + \\
& + \sum_m [(n_k n_m j_{km} - n_e n_i n_m j_{ek}^m) + \\
& + \sum_n (n_k n_m j_{kn}^m - n_n n_m j_{nk}^m)] = 0.
\end{aligned} \tag{7}$$

Summation with respect to \underline{n} is carried out over the group of associated levels. This process takes into consideration all the collisions which move particles within this set of levels.

If collisions with electrons are predominant, we derive a Boltzmann distribution (for T_e) within the set of states (Ref. 5):

$$n_k = n_{k+1} \frac{j_{k, k+1}^e}{j_{k+1, k}^e} = \dots = n_e n_i \frac{j_{ek}^e}{j_{ke}^e}. \tag{8}$$

If on the contrary, however, atom-atom collisions predominate, then these relationships are satisfied:

$$\begin{aligned}
& \sum_m [(n_k n_m j_{km} - n_e n_i n_m j_{ek}^m) + \\
& + \sum_n (n_k n_m j_{kn}^m - n_n n_m j_{nk}^m)] = 0.
\end{aligned} \tag{9}$$

The discrepancy between T_a and T_e gives a complex particle distribution in the set even in this extreme case.

Let us simplify the system of equations derived earlier by using equation (8) - i.e., by assuming that the link between the excited and ionized states is forged by electron shock. Let us include in the set of combined states all the excited levels and the continuous spectrum. This is feasible if there are no excited states in the vicinity of the basic state. /344

We shall then obtain

$$\begin{aligned}
\frac{d}{dx}(u_1 v) &= -\frac{d}{dx} \left[v \left(u_e + \sum_{k \geq 1} u_k \right) \right] = \\
&= -\frac{d}{dx} \left[v \left(u_e + u_e n_i \sum_{k \geq 1} \frac{j_{k, k+1}^e}{j_{k+1, k}^e} \right) \right] = S_1 = \\
&= -(u_1 n_i j_{1e}^* - u_e^2 n_i j_{1e}^*) - (u_2^2 j_{2e}^* - u_e n_i u_2 j_{2e}^*) - \\
&\quad - (P_1 - n_e n_i u_{e1}^*),
\end{aligned} \tag{10}$$

where

$$\begin{aligned}
 j_{n1}^* &= j_{n1} + \sum_n j_{n1}^e, \quad j_{e1}^* = \sum_n j_{n1}^e \frac{j_{en}^e}{j_{ne}^e}, \\
 j_{n1}^* &= j_{n1} + \sum_n j_{n1}^e, \quad a_{e1}^* = a_{e1} + \sum_n a_{n1} \frac{j_{en}^e}{j_{ne}^e}, \\
 j_{e1}^* &= j_{e1} + \sum_{n \geq 1} (j_{n1}^e - j_{ne}^e - j_{nm}^e) \frac{j_{en}^e}{j_{ne}^e}, \\
 q_{e1}^* &= \sum_{n \geq 1} \frac{j_{en}^e}{j_{ne}^e} \left(j_{n1}^e + \frac{j_{en}^e}{j_{ne}^e} j_{n1}^m \right), \\
 -\frac{d}{dx} \left(\frac{3}{2} kT_e n_{e1} \right) + kT_e n_e \frac{dv}{dx} &= S_{ee} = \sum_m n_m n_e (Q_{ne} - F_{me}) + \\
 + W_{ee} - n_e n_i \sum_k q_{k1} a_{ek} - U_i (n_i n_e j_{ie}^* - n_e^2 n_i j_{ie}^*) + n_i^2 q_{i1} j_{ie}^* + \\
 + n_e n_i n_1 \left[\sum_{k \geq 1} \frac{j_{ke}^e}{j_{ke}^e} (q_{k1} j_{he}^* + q_{1k} j_{ie}^*) - \sum_k q_{k1} j_{ek}^* \right] + \\
 + n_e^2 n_i^2 \sum_{m \geq 1} \frac{j_{em}^e}{j_{me}^e} \left[\sum_{k \geq 1} q_{km} \frac{j_{ke}^e}{j_{ke}^e} j_{ke}^m - \right. \\
 \left. - \sum_k q_{km} j_{ek}^m \right] + \sum_{k \geq 1} (U_i - U_k) s_k, \tag{11}
 \end{aligned}$$

$$\begin{aligned}
 \frac{d}{dx} \left[\left(\frac{5}{2} kT_e + \frac{m_e v^2}{2} \right) \left(n_i + \sum_k n_k \right) v \right] + v \frac{d(kT_e n_e)}{dx} &= -Q - S_{ee} + U_i S_1 + \\
 + \sum_{k \geq 1} (U_i - U_k) \frac{d}{dx} \left(n_e n_i \frac{j_{ke}^e}{j_{ke}^e} v \right). \tag{12}
 \end{aligned}$$

Equation (10) is far more complex than any of the equations of the original system (1). In it, as in equations (11) and (12), all the coefficients for n_e , n_i , and n_1 depend only on temperatures T_a , T_e and may be calculated. In equation (11), s_k is the algebraic sum of the numbers of transitions to level k resulting from collisions with electrons. As a rule $\sum_{k \geq 1} (U_i - U_k) s_k$ is a small quantity.

By taking advantage of the similarity of the upper excited states /345 with hydrogen, we may estimate $\sum_{k=1}^{\tilde{k}} n_k$, where \tilde{k} is the last of the discrete states realized in the plasma:

$$\frac{1}{n_e^2} \sum_{k=1}^{\tilde{k}} n_k \approx \frac{Ry}{2(2\pi m_e kT_e)^{3/2}} \int_{U_i}^{U_i + kT_e} x^{-3/2} e^{-x} dx. \tag{13}$$

If T_e is not very large, then $\sum_{k>1} n_k \ll n_e$. This reflects the pre-
 cominance of the statistical weight of the continuous spectrum over that
 of the discrete states. Let us assume that ionization and excitation are
 effectuated principally by electron impact, while $j_{ie}^e \ll \sum_k j_{ik}^e$. If
 $\sum_{k>1} n_k \ll n_e$, then almost all the newly-formed excited atoms must become
 ionized, and this approximates the "instantaneous ionization" adopted in
 (Ref. 1 and 2). In the regimes examined in (Ref. 1 and 2), the conditions
 of "instantaneous ionization" were satisfied.

Behind the shock-wave front, equation (11) quickly becomes quasi-
 stationary - i.e., the left-side terms with the derivatives dT_e/dx and
 dv/dx may be disregarded. Under certain, frequently-occurring conditions,
 moreover, the derivatives dn_k/dx are small, when $k > 1$. The equations are
 then simplified to

$$\begin{aligned} \frac{da}{dx} &= -\frac{1}{nv} S_e, \\ S_e - \frac{3}{2} kT_e S_e &= 0. \end{aligned} \quad (14)$$

Here the degree of ionization $\alpha = n_e/n$ has been introduced, and the con-
 servation condition $nv = \text{const.}$ taken into account; $n = n_1 + \sum_k n_k$ is the
 total number of heavy particles. As a rule, equation (12) can also be
 simplified:

$$nv \frac{d}{dx} \left\{ \frac{5}{2} kT_e + a kT_e \right\} = -Q - S_e - C S_e.$$

Combining the levels to the limit has simplified the problem by
 allowing us to omit from our consideration the kinetics of individual
 excited-state formation and destruction. What can stand in the way of this
 combination?

It is the impacts which bind the states into a set. If the frequency
 of the radiation processes is much less than the frequency of these impacts,

then de-excitation does not disturb particle distribution in the set. We should note that this rigid condition is not necessary (Ref. 5).

When traveling behind a shock-wave, a gas element comes under various conditions. The relaxation time corresponding to the travel of the set particles must be much less than the total relaxation time. This can be brought about by combining layers which are similar in terms of energy.

If we neglect the radiation transitions into the basic state, then any system of combining levels which rigidly links excited atoms and electrons permits us at the beginning of relaxation to take into account only the entry of the particles into the set. The population of the excited levels proves to be slight in comparison to the Boltzmann population computed with respect to the basic state. Therefore, collisions of the second kind, which remove particles from the set of states, as well as recombination, may be neglected right up to degrees of ionization which are very close to equilibrium. At this stage, the set of levels is a /346 passive reservoir, since atoms which get into it cannot get out.

Considering de-excitation at length, we cannot arrive at a general conclusion, since the corresponding direct process - absorption of the radiation of the remaining gas volume - is not always sufficiently strong. But, inasmuch as the concentration of excited atoms is low, we may also in a number of cases in the first stage disregard de-excitation, in comparison with ionization and excitation by collisions.

Behind strong shock-waves, the degrees of ionization in the region near equilibrium are great, and the relationships in expression (8) are valid. Immediately behind the front, on the other hand, atom-atom collisions may predominate. The cross-sections of these collisions are generally

unknown. The remark has already been made, however, that in a number of cases at the beginning of relaxation it is not essential, as regards the development of the relaxation process, to have an idea of the nature of particle distribution within the level set. This significantly simplifies the task.

It is at times advisable to distinguish two sets of levels. Thus, if there are low-lying excited levels in the vicinity of the basic level, they may be combined with the latter.

In concluding our remarks on the manner of solving the kinetics equations, let us underscore the need for a careful check of this very possibility of combining levels into a unit.

Relaxation Behind Powerful Waves in Air

When $v_1 \gg 10$ km/sec, molecules dissociate very rapidly (see Appendix), and thereafter their concentration is negligibly small. For this reason, we are dealing with relaxation in a mixture of O and N. Various collisions result in the formation of the ions N^+ , O^+ , NO^+ , N_2^+ , O_2^+ . Since the ions are in quasi-equilibrium with each other, it turns out that concentrations of molecular ions are insignificantly small.

Let us introduce our notation. Atom concentrations are n_O , n_N . If we have in mind a certain k^{th} state, the notation is n_{O_k} , n_{N_k} . Ion concentrations are n_N^+ , n_O^+ ; their sum is n_i^* . The degree of ionization is $a = n_e/n$, $n = n_O + n_N + n_i$.

* Concentrations of molecular ions may be found as small additions by means of the relationship $(n_O + n_O^+ + n_{NO}^+ + 2n_{O_2}^+)/ (n_N + n_N^+ + n_{NO}^+ + 2n_{N_2}^+) = 0.21/0.79$ and equations such as equation (6): $n_{NO}^+ = n_N^+ n_O K_1 = n_N n_O^+ K_2$, $n_{N_2}^+ = n_N n_N^+ K_4$, $n_{O_2}^+ = n_O^+ n_O K_3$.

The condition $\rho v = \text{const.}$ can be reduced to $nv = \text{const.}$ Then

$$\begin{aligned}\frac{d(n_e v)}{dx} &= S_e = -\frac{d}{dx} \sum_k (n_{N_k} + n_{O_k}) v \approx \\ &\approx -\frac{d}{dx} \sum_{k=1}^3 (n_{N_k} + n_{O_k}) v.\end{aligned}\quad (15)$$

In the solution of specific problems, the lack of information on atom-atom collisions frequently prevents the kinetics of the excited states from being taken into account in the first stage of relaxation. This difficulty may be avoided in the case of air, because atom-atom excitation cannot compete with associative ionization. Therefore, electrons are formed, escaping the upper excited states. The distribution of atoms over excited states is at this stage of no interest, as regards the development of ionization.

At larger values of n_e , ionization becomes stepped, but even then it may be shown that two sets of states, within which equilibrium is maintained by electron impact, are formed among the atoms. The first is comprised of the basic state and the two adjacent states; the second - of the remaining states and the continuous spectrum.

Let us write the system of equations for this pattern of combined /347 levels. We shall take electron processes and associative ionization into consideration. The electron source is

$$\begin{aligned}S_e \approx \sum_{k=1}^3 \{ & (n_{N_k} n_e j_{ke}^{e*} - n_e^2 n_{N^+} j_{ek}^{e*}) + (n_{O_k} n_e i_{ke}^{e*} - n_e^2 n_{O^+} i_{ek}^{e*}) + \\ & + (P_{N_k} - n_e n_{N^+} a_{ek}^*) + (P_{O_k} - n_e n_{O^+} \beta_{ek}^*) + \\ & + (n_{N_k} n_{N^+} j_{ke}^{1*} - n_e n_{N^+} j_{ek}^{1*}) + (n_{O_k} n_{O^+} i_{ke}^{1*} - n_e n_{O^+} i_{ek}^{1*}) + \\ & + (n_{N_k} n_{O^+} g_{ke}^{1*} - n_{N^+} n_{O^+} g_{ek}^{1*}) \}.\end{aligned}\quad (16)$$

In contrast to expression (10), summation at j_{ek}^{e*} , j_{ke}^{e*} , a_{ek}^* is then accomplished for $n > 3$. Furthermore, $j_{ie}^{1*} = \frac{1}{2} \sum_{n=1}^3 \frac{j_{in}^e}{j_{n1}^e} j_{ie}^{1*}$, $j_{ei}^{1*} = \frac{K_i}{2} \sum_{n=1}^3 j_{ei}^{1*}$. The notation j_{ke}^e , j_{ke}^1 , j_{el}^n , a_{ek} , etc. is left for the N atom; i_{ke}^e , i_{ke}^1 , i_{el}^n , β_{ek} ,

etc., is the corresponding notation for the O atom. For example,

$$i_{e1}^{1*} = \frac{1}{2} \sum_{n=1}^3 \frac{i_{1n}^e}{i_{n1}^e} i_{e1}^n.$$

The coefficient

$$g_{ie}^n \cdot g_{ie}^{1*} = \sum_{n=1}^3 \frac{i_{1n}^e}{i_{n1}^e} g_{ie}^n, \quad g_{e1}^{1*} = K_1 \sum_{n=1}^3 g_{e1}^n.$$

is introduced for the process of forming NO^+ . Radiation absorption is taken into account by P_{N_k} and P_{O_k} .

The source of electron energy is

$$\begin{aligned} S_{ee} \approx & \sum_m n_e n_m Q_{me} - \sum_{k=1}^3 \left[U_N (n_e n_{N_k} j_{he}^{e*} - n_e^2 n_{N_k}^+ j_{ek}^{e*}) + \right. \\ & + U_O (n_e n_{O_k} i_{he}^{e*} - n_e^2 n_{O_k}^+ i_{ek}^{e*}) - \left(\frac{1}{2} n_{N_k}^2 \sum_{n=1}^3 \frac{j_{kn}^e}{j_{nk}^e} j_{he}^n \varphi_{kn}^N - \right. \\ & - n_e n_{N_k}^+ n_{N_k} \frac{K_4}{2} \sum_{n=1}^3 j_{ek}^n \varphi_{nk}^N \left. \right) - \left(\frac{1}{2} n_{O_k}^2 \sum_{n=1}^3 \frac{i_{kn}^e}{i_{nk}^e} i_{he}^n \varphi_{kn}^O - \right. \\ & - n_e n_{O_k}^+ n_{O_k} \frac{K_5}{2} \sum_{n=1}^3 i_{ek}^n \varphi_{nk}^O \left. \right) - \left(n_{O_k} n_{N_k} \sum_{n=1}^3 \frac{i_{kn}^e}{i_{nk}^e} g_{he}^n \varphi_{kn}^{NO} - \right. \\ & \left. - n_e n_{O_k}^+ n_{N_k} K_1 \sum_{n=1}^3 g_{ek}^n \varphi_{nk}^{NO} \right) + n_e n_{N_k}^+ \varphi_{N_k}^N \alpha_k + n_e n_{O_k}^+ \varphi_{O_k}^O \beta_k \left. \right], \end{aligned} \quad (17)$$

where U_O and U_N designate the ionization energy of the oxygen and nitrogen atoms.

This system of kinetics equations (to which must be added an equation for T_a) is integrodifferential. Substantial computation difficulties must be overcome to solve this system, but in a number of cases it may be simplified.

At the beginning of relaxation, there are certain nonessential processes. In addition, $n_N \approx 0.79n(1 - \alpha)$, $n_O \approx 0.21n(1 - \alpha)$. We then have

$$\begin{aligned} \frac{S_e}{n^2} = & \alpha(1 - \alpha)(0.79j_{he}^{e*} + 0.21i_{he}^{e*}) + (1 - \alpha)^2(0.79^2j_{he}^{1**} + \\ & + 0.79 \cdot 0.21j_{he}^{1**} + 0.21^2i_{he}^{1**}) + \sum_{k=1}^3 \left[\left(P_{N_k} - \alpha^2 \frac{n_{N_k}^+}{n_e} \alpha_{N_k}^{**} \right) + \right. \\ & \left. + \left(P_{O_k} - \alpha^2 \frac{n_{O_k}^+}{n_e} \beta_{O_k}^{**} \right) \right], \end{aligned} \quad (18)$$

$$\begin{aligned} \frac{S_{12}}{n^2} = & a^2(Q_1 + a(1-a)(0.79Q_{N_2} + 0.21Q_{N_2}) - a(1-a)(U_N \cdot 0.79j_{N_2}^{***} + \\ & + U_O \cdot 0.21j_{N_2}^{***}) + (1-a)^2(q_N \cdot 0.79j_{N_2}^{***} + q_N^{(0)} \cdot 0.79 \cdot 0.21j_{N_2}^{***} + \\ & + q_N^{(0)} \cdot 0.21j_{N_2}^{***})). \end{aligned} \quad (19)$$

Here the following notation is used:

$$\begin{aligned} j_{12}^{***} &= \left(1 + \frac{j_{21}^e}{j_{12}^e} + \frac{j_{31}^e}{j_{13}^e}\right)^{-1} \sum_{k=1}^3 \frac{j_{1k}^e}{j_{1k}^e} j_{k2}^{**}, \\ j_{11}^{***} &= \left(1 + \frac{j_{21}^e}{j_{12}^e} + \frac{j_{31}^e}{j_{13}^e}\right)^{-2} \sum_{k=1}^3 \frac{j_{1k}^e}{j_{1k}^e} j_{k1}^{**}, \\ u_{12}^{**} &= \sum_{k=1}^3 u_{ek}^*, \\ \bar{q}_N j_{N_2}^{***} &= \frac{1}{2} \left(1 + \frac{j_{21}^e}{j_{12}^e} + \frac{j_{31}^e}{j_{13}^e}\right)^{-2} \sum_{k, n=1}^3 \frac{j_{1n}^e j_{1k}^e}{j_{1n}^e j_{1k}^e} j_{kn}^{**} q_{kn}^N. \end{aligned}$$

The remaining notation is similarly introduced.

It may be demonstrated that when, under our conditions, $\alpha \leq 0.3\alpha_{eq}$ (subscript eq refers to parameters of equilibrium attainable when there are no losses) impacts of the second kind and recombination, transferring particles from the upper set into the lower, may be neglected, as well as radiation processes, both in kinetics and in energy balance. The conservation equations are accordingly simplified.

Computing Relaxation in Air

Relaxation for shock waves of velocities $v_1 \geq 10$ km/sec is determined by the processes which follow. At first, associative ionization $N + O = NO^+ + e$, $N + N = N_2^+ + e$, $O + O = O_2^+ + e$ prevails. With the growth of n_e , the role of stepped ionization by electrons also increases, and the velocity of ionization is determined by electron temperature. It is principally supported by elastic electron-ion collisions. At the beginning of relaxation, the electrons, which were already "hot" to a significant degree, become further heated by elastic collisions with atoms.

Let us discuss the velocities which we chose for the different processes.

By utilizing experimental data on dissociative recombination, we can find the velocity of associative ionization. The recombination coefficients of the ions N_2^+ , NO^+ , O_2^+ measured at low temperatures are close in size and are large. This indicates that in every case the potential curves of the recombination products and of the molecular ion intersect near the ion's basic vibrational level, $K = 0$ (for N_2^+ this /349 point of intersection is still unknown, which is obviously an indication of the general lack of information on unstable states). With an intersection of this type, the recombination coefficients usually depend on T , as $T^{-3/2}$. Let us use this for extrapolation to larger values of T :

$$j_{N_2^+} = 6 \cdot 10^{-2} T^{-3/2}, \quad i_{N_2^+} = 4 \cdot 10^{-2} T^{-3/2}, \quad g_{N_2^+} = 3 \cdot 10^{-2} T^{-3/2} \text{ cm}^2/\text{sec}. \quad (20)$$

These figures are taken from (Ref. 4), where a similar line of reasoning is followed. Because of the impossibility of accurately determining the recombination products (e.g., one of the N atoms may be weakly excited), it is assumed in expression (20) that they are atoms in basic states. At large values of T , this assumption does not have too great an effect on ionization.

A greater error in the growth of T is apparently caused by the following effects. (1) The dependence of $T^{-3/2}$ does not account for the change in population of the lower vibrational levels, and this reduces the coefficient of recombination. (2) The reaction also goes through other higher-situated points of intersection, and this increases the coefficient of recombination.

As a light particle, the electron falls heir to all the energy above the threshold energy. When the potential curves intersect in the vicinity of $K = 0$, the cross-section of the process rapidly decreases as the energy

risers. By virtue of this, the value of $\bar{\phi}$ is small. In other cases, the cross-section may be slightly dependent on energy, and the problem is complicated because an ion may form at various K levels. A rough estimate shows that $\bar{\phi}$ does not exceed kT_a . The indeterminacy of $\bar{\phi}$ is not significant, because electron temperature at the beginning of relaxation does not affect ionization velocity.

Cross-sections to calculate j_{ie}^{e*} , j_{2e}^{e*} , i_{ie}^{e*} , etc. are found by the method proposed in (Ref. 6 and 7), which most fully accounts for the exact behavior of the cross-section in the threshold vicinity and at great energies. In the interval $T_e = 8000$ to $18,000^\circ K$, we have:

$$j_{ie}^{e*} = 3 \cdot 10^{-10} T_e^{-1/2} e^{-45000/T_e}, \quad i_{ie}^{e*} = 1.8 \cdot 10^{-10} T_e^{-1/2} e^{-45000/T_e} \text{ cm}^2/\text{sec}. \quad (21)$$

These coefficients are adequately precise when we consider that the rate of excitation by electrons is to a considerable degree determined by the transfer to them of energy from heavy particles (Ref. 7).

We find the transfer of energy from ions to electrons in the usual way, i.e.,

$$Q_{ie} = \frac{2e^4 \sqrt{2\pi m_e}}{m_i} \frac{kT_a - kT_e}{(kT_e)^{3/2}} \left[\ln \frac{3(kT_e)^2}{8\pi e^2 n_e} + 1 \right].$$

For atom-electron collisions it was found that

$$Q_{ae} = \frac{4m_e}{m_a} \sqrt{\frac{8kT_e}{\pi m_e}} \sigma (kT_a - kT_e) \{1 - (1 + T_e/T_a)^{-1/2}\},$$

where $\sigma = 6 \cdot 10^{-16} \text{ cm}^2$ for N and $5.5 \cdot 10^{-16}$ for O; $T_y = 3.1 \cdot 10^4$ and $1.2 \cdot 10^4$ °K, respectively. These constants appeared during approximation of the cross-sections measured in (Ref. 8).

A Maxwell distribution with respect to velocity was assumed for the electrons. Calculations showed that the Maxwell distribution occurs at

values of n_e where excitation and ionization by electrons becomes substantial, and Maxwell distribution occurs.

We found α_{ek}^* and β_{ek}^* by means of transition probabilities derived by the quantum defect method. In the interval $T_e = (8 \div 20) \cdot 10^2$ °K, we have

$$\alpha_{ek}^{**} = 5.0 \cdot 10^{-8} e^{-1.6 \cdot 10^{-4} T_e} + 1.2 \cdot 10^{-11} e^{-1.6 \cdot 10^{-4} T_e} T_e^{1/2} \text{ sec.} \quad (22)$$

The value of β_{ei}^{**} is similar.

Associative ionization is such a powerful mechanism of primary ionization that we may refrain from considering absorption in the radiation /350 relaxation zone of the rest of the gas volume. By assuming that all the photons emitted toward the front and corresponding to transitions to the three lower levels are effectively absorbed, we may set an upper limit to the role of radiation. Associative ionization in argon proceeds slowly, and the radiation processes are significant (Ref. 2).

Kinetics equations can be written for the case in which equilibrium within both sets of levels is supported by electron impact. We will show that the nature of distribution within the sets begins to have an effect only when the hypothesis adopted proves to be true.

Let us compare the lifetime of state τ with the time interval between impacts which transfer the atom to one of the adjacent levels of τ_{imp} . Regardless of whether we find cross-sections by Milford's method (Ref. 6) or use quasi-classical expressions (Ref. 9), it turns out that with the values of n_e of interest to us and with values of $p_1 > 10^{-5}$ atm, the relation $\tau_{imp}/\tau \ll 1$ holds. In addition, the efficiency of the electron-atom and atom-atom collisions which transport particles between the upper levels must also be compared. Calculations have demonstrated that at values of

n_e - when the type of combination of levels in the set is essential - the atom-atom collisions may be disregarded.

The excited states of the basic configuration are metastable. The electron-atom cross-sections are large enough (Ref. 10) to maintain equilibrium within the lower level set at the values of α , which we need.

Relaxation in argon has previously been studied (Ref. 2). It began with a certain finite degree of ionization. The large values of p_1 , even with these values of α , allowed the upper levels to be combined, i.e., the assumption as to ionization of the excited states was justified.

The kinetics equations were solved up to $\alpha = 0.5 \alpha_{eq}$. It proved to be possible to leave out of consideration de-excitation, impacts of the second kind, and recombination. The role of de-excitation in equation (14), estimated by means of equation (24), reached a maximum of 30%. In reality, the lines which made the greatest contribution to equation (22) are intensely reabsorbed, i.e., not only must the radiation of a given volume element of gas, but also its absorption of the radiation of the rest of the gas, be taken into account. This may be done approximately by introducing the effective lifetimes, instead of a lifetime τ of the isolated atoms, into the determination of α_{ek}^* and β_{ek}^* (Ref. 11). It is found that such effective values of α_{ek}^* and β_{ek}^* are lower in order of magnitude than equation (22). Radiation cooling in this relaxation sector could also be neglected, i.e., $Q = 0$.

Discussion of Results

The above analysis of the elemental processes shows that up to $\alpha = 0.5 \alpha_{eq}$, relaxation in air takes place according to a binary

system*. This makes it possible to formulate a universal profile of non-equilibrium parameters as a function of $p_1 x$ for a given v_1 . (Let us recall that α_{eq} depends on p_1 . The above-derived solutions are valid for $\alpha \leq 0.5\alpha_{eq}$. Consequently, the profiles formulated as a function of $p_1 x$ are valid for various values of p_1 in different $p_1 x$ ranges. Figure 1 gives, as examples, profiles of α , T_a , and T_e when $v_1 = 12$ km/sec.

No great significance must be attributed to the region of small values of ** in Figure 1. In reality, there is a slight overlap of ionization and dissociation regions (nonessential to the development of relaxation). The imprecise determination of $\bar{\phi}$ leads, moreover, to indeterminacy in T_e . The computations with different values of $\bar{\phi}$ gave no perceptibly different results, although strong variations were experienced with small xT_e (Figure 1 presents the case $\bar{\phi} = 0$). For the same reason, it is not important that electron thermal conductivity tends to raise T_e in the region of small values of x .

We have previously discussed the dependence of T_a and T_e on x /351
(Ref. 2)

Figure 2 represents the dependence of $p_1 t$ on velocity v_1 (t is the relaxation time in the laboratory system of coordinates).

Investigations of relaxation in air were previously conducted for

* (Ref. 4, 12, and 13), which investigate the lack of equilibrium behind a shock-wave in air for $v_1 < 9$ mm/sec, also noted the binary nature of relaxation, but the relaxation process in argon (Ref. 2) was not binary, due to the substantial effect on relaxation of radiation from an equilibrium zone.

** Translator's note: Illegible in original foreign text.

shock-waves of velocities $v_1 \leq 9$ km/sec*. Measurements were made of the length of the ionization relaxation zone -- the distance at which the electron concentration drastically increases and then arrives at quasi-equilibrium with a gas state which varies slowly in the process of dissociation relaxation**. Right up to $v_1 = 9$ km/sec, the relaxation length was determined by the kinetics of molecular decay. Figure 2 presents the results of this work.

From Figure 2 it follows that in the $v_1 = 9 \div 10$ km/sec range, the nature of the relaxation abruptly changes ***. For $v_1 > 10$ km/sec, the entire relaxation time is determined by the kinetics of relaxation. In the $v_1 = 9 \div 10$ km/sec range, the calculation of relaxation is a complex problem, but it is clear that the ionization relaxation time must lengthen

* V. A. Bronshten studied relaxation behind the front of a powerful shock-wave in air (Ref. 16). It was assumed that ionization came from collisions with electrons (atom-atom collisions were not considered). It was thus assumed that Boltzmann's law defined the ratio of atom concentrations in excited and basic states over the entire nonequilibrium region. It was assumed that such a high concentration of excited states was created by radiation absorption. Excitation by impact was not taken into account. An elementary estimate shows that the energy emitted by the shock wave is clearly inadequate to support the Boltzmann distribution under the conditions of the nonequilibrium zone of the shock-wave. In addition, thermodynamically contradictory expressions were utilized as coefficients of triple recombination and ionization by electron impact. Since the elementary ionization processes are incorrectly considered in (Ref. 16), it is hard to assume that the nonequilibrium zone characteristics derived by Bronshten are correct in order of magnitude.

** We should note that at such velocities this quasi-equilibrium of n_e exceeds its equilibrium value. The calculation made for $v_1 \leq 9$ km/sec indicated that at higher values of v_1 , this excess disappears (Ref. 4).

*** In the $v_1 \div 9$ to 10 km/sec range, the value of α_{eq} did in fact change by a factor of 10 (in the 10-11 km/sec range by a factor of 2), and the ionization energy comprised a noticeable contribution to enthalpy.

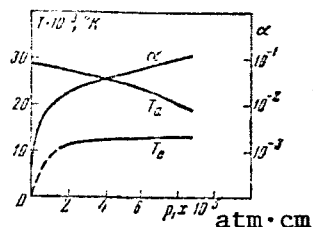


Figure 1

Parameter Profile of Nonequilibrium Gas Behind Shock Wave

$v_1 = 12$ km/sec. Result does not depend on pressure before front p_1 [right up to $\alpha = 0.5 \alpha_{eq}$; $\alpha_{eq} = \alpha_{eq}(p_1)$]. Because of the indeterminacy of T_e at low values of x (see text), this sector is indicated by a broken line in Figure 1.

as v_1 increases. This result has nothing to do with the accuracy with which associative ionization velocities are established. The employment of other values for these quantities alters the absolute values of the ionization relaxation time, but preserves their nonmonotonic nature. At the same time, we assume that an abrupt change in quantitative results should not be the consequence of greater precision in the reaction velocity values used.

It is to be noted that the manner in which the theses underlying our consideration are satisfied improves as velocity v_1 becomes higher. In this sense, the case in which $v_1 \approx 10$ km/sec is the case most liable to /352 the effect of various unfavorable factors, such as incompleteness of dissociation relaxation and discrepancies in associative ionization effectiveness.

This article does not examine matters involving gas glow behind the shock-wave. It must be borne in mind that often the role of certain constituents in kinetics and in shock-wave radiation is entirely different. A low concentration of any strongly-emissive gas constituent may not have

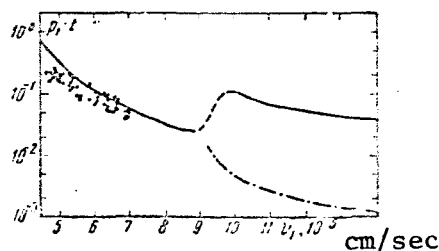


Figure 2

Dependence of Product of Relaxation Period t (in laboratory system)
by Pre-front Pressure p_1 (in units of μ sec·mm Hg) on
Shock-wave Velocity

$p_1 = 0.02$ mm Hg. Solid line - ionization relaxation calculation
[at $v_1 \leq 9$ (Ref. 4); at $v_1 \geq 10$ (our work)]; dotted line -
experimental findings (Ref. 14); --- - estimate in Appendix.

any effect on kinetics at all. For example, if charge exchange processes are fast enough, the value of $n_{N_2^+}$ may be comparatively large and exceed its value in equilibrium, while the atomic ion concentration meantime remains considerably smaller. Therefore, despite the rigid link between the concentrations of excited atoms and electrons throughout most of the relaxation length, the problem of emissive particle concentration cannot be considered to be solved. In addition, in the first relaxation sector we are not adequately familiar with the concentrations of excited atoms, and there is a certain number of still undissociated molecules. Without affecting kinetics, these two latter facts can nevertheless be very important with regard to luminescence behind the shock wave, but as v_1 becomes higher, their role should decrease.

We have examined the region of ionization relaxation in which opposing processes may be disregarded. The region where the gas passes through a state approximating equilibrium is very complex, and here the opposing

processes are very significant. The last stage of relaxation moreover proceeds in a gas which may be appreciably cooled because of radiation yield. If p is large, then the gas has time to reach equilibrium before radiation cooling significantly lowers its internal energy. Equilibrium will be further maintained, but at a gradually decreasing temperature (Ref. 15). It is, however, possible that radiation yield will prove to be substantial even in the last stage of relaxation. In this case, equilibrium will in general not be attained because of the continuously-uncompensated combination of excited and ionized states (Ref. 5). If, however, the efficiency of the impact processes is great enough, the gas will arrive at a state of local equilibrium, but at temperatures below those calculated on the assumption that there will be no radiation losses.

In a paper which will follow, we hope to examine the whole relaxation region by taking advantage of the general equations written above.

The authors are grateful to Yu. P. Rayzer for his valuable comments.

APPENDIX

Dissociative Relaxation at Large Values of v_2

It was noted in (Ref. 3) that the length of the dissociative relaxation zone behind powerful shock-waves is very short. The molecules dissociate immediately in collisions between atoms and among themselves. Let us cite the appropriate estimates.

Under our conditions, O_2 molecules dissociate practically instantaneously. We will examine the kinetics of N_2 dissociation. Let us introduce:

$$\beta = n_N / (n_N + 2n_O), \quad m' = 2m_N + \xi m_O, \quad \xi = 0.21 / 0.79.$$

Then

$$\partial \rho / \partial x = m' (2 \rho_1 v_1)^{-1} S_N(x). \quad (23)$$

In the symbol S_N - the source of nitrogen atoms - we take into account the processes



Introducing the notation $k^{(0)}$, $k^{(N)}$, $k^{(N_2)}$ for their velocities, we get

$$S_N = \{ (n_N + n_O + n_N) / (1 + 2\xi + \beta) \}^2 (1 - \beta) \times \\ \times [2\xi^2 k^{(N)} + 2\xi^2 k^{(O)} + (1 - \beta) k^{(N_2)}]. \quad (25)$$

Equation (23) is integrated by taking into account conservation conditions /353

$$kT = (H_0 m' - \xi D_O - \beta D_N) \left(\frac{9}{2} + 5\xi + \frac{\beta}{2} \right), \quad p \approx p_0. \quad (26)$$

We have assumed that the vibrational relaxation of N_2 has finished. This assumption does not affect the result.

Figure 2 gives the findings of the calculation made using dissociation velocities taken from the survey in (Ref. 13). Time t_{dis} corresponds to the point at which the molecular fraction is 0.08 of all the particles. At velocities of $v_1 \geq 10$ km/sec, the value of t_{dis} is comparatively small.

Associative ionization also proceeds simultaneously with dissociation, but the degrees of ionization achieved in time t_{dis} are slight, and do not affect the gas parameters. This also holds true when $v_1 \leq 9$ (Ref. 4). We will compute the degree of ionization reached during dissociation:

$$\alpha(x) = m' \{ \rho_1 v_1 (1 + 2\xi + \beta) \}^{-1} \int_0^x S_e dx. \quad (27)$$

when $v_1 = 10$ km/sec, $\alpha \approx 1.7 \cdot 10^{-3}$ is reached in time t_{dis} . This is a small quantity, and does not influence the succeeding course of relaxation.

The case of $v_1 = 9$ km/sec was also studied. Here the dissociation of N_2 by the formation of NO plays just as important a role as in equation (24). Ionization relaxation proceeds simultaneously with dissociation

relaxation. The ionization relaxation characteristics derived, as was to be expected, agreed with those quoted in (Ref. 4).

Note in proof. After this paper was sent to press, an article by Allen, R. A., Textoris, A., and Wilson, J. appeared (J. Quant. Spectr. Radiat. Transf., Vol. 5, p. 95, 1965) which measured relaxation periods. It gave an ionization relaxation time of $t \approx 1_{\mu}$ sec for a shock-wave of $v_1 = 10.9$ and 11.25 km/sec and $p_1 = 0.1$ mm Hg, which gives good confirmation of our conclusions.

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